Quality Assessment Report for Water Quality Monitoring

October – December 2024

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INTRODUCTION

This report is an assessment of the South Florida Water Management District (SFWMD) field sampling and laboratory analysis for total phosphorus (TP) in surface water, primarily for the projects and their associated stations as shown in **Table 1** from October 1, 2024, through December 31, 2024. The analysis reflects the status of the data at the time of download and does not account for changes made to the data after February 11, 2025.

Table 1. Projects and associated stations.

Project Name	Project ID	Stations
Everglades National Park Inflows North	PIN	S12A, S12B, S12C, S12D, S333, S333N, S355A, S355B, and S356-334
Everglades National Park Inflows East	PIE	G737, S332DX, S18C, and S328
Everglades Protection Area	EVPA	LOX3, LOX4, LOX5, LOX6, LOX7, LOX8, LOX9, LOX10, LOX11, LOX12, LOX13, LOX14, LOX15, and LOX16

The Water Quality Monitoring Section (WQM) *Field Quality Manual* (SFWMD-FIELD-QM-001) and *Field Sampling Manual* (SFWMD-FIELD-FSM-001) provided the quality system requirements, and the field sampling procedures were followed in field sample collection from October 1, 2024 to December 31, 2024. The Analytical Services Section's *Chemistry Laboratory Quality Manual* (SFWMD-LAB-QM-001) provides the guidance and requirements for preparing and analyzing laboratory samples, as well as data verification and validation. The *Field Sampling Quality Assessment* and *Laboratory Analysis Quality Assessment* sections in this report provide a comprehensive evaluation and validation of the TP results for surface water samples collected from the locations and timeframe described above.

To prepare this report, a Microsoft Excel workbook named "qa_report_oct_dec_2024_data.xlsx" was also created, containing all TP results obtained from DBHYDRO, SFWMD's corporate environmental database, for all sampling events. This includes grab samples collected for the projects/stations listed above during the period specified in this report. The Excel workbook will be referred to as the Reference Data Set (RDS) throughout this report and both of the documents are available for reference on the Everglades Technical Oversight Committee (TOC) website (https://www.sfwmd.gov/our-work/toc). TP analyses were completed at the SFWMD Analytical Services Chemistry Laboratory (Florida Department of Health Identification # E46077).

If available, TP sample results for biannual laboratory proficiency testing as required by the National Environmental Laboratory Accreditation Program (NELAP) or results from other laboratory performance evaluation studies completed during the period specified in this report will also be included.

FIELD SAMPLING QUALITY ASSESSMENT

SAMPLE COLLECTION

All samples were collected by WQM staff. A total of 45 sampling events were conducted that included collection of samples for the projects/locations and timeframe described in the *Introduction* to this report. A complete list of the laboratory work orders obtained from the Laboratory Information Management System (LIMS) for these sampling events is shown in **Table 2**. The table details the work order identifiers, work order numbers, project codes, and sample collection dates.

Table 2. Sampling events for the reporting period.

Work Order Identifier	Work Order	Project [a]	Date Collected
P153820	92931	PIN	10/01/2024
P153868	92955	PIE	10/02/2024
P153904	92973	PIE	10/02/2024
P153900	92971	EVPA	10/02/2024
P153161	92597	EVPA	10/03/2024
P152164	92095	PIE	10/08/2024
P152150	92088	PIE	10/08/2024
P153824	92932	PIN	10/08/2024
P152111	92068	PIN	10/15/2024
P152539	92280	PIE	10/15/2024
P152527	92274	PIE	10/16/2024
P153911	92974	PIE	10/22/2024
P153843	92937	PIN	10/22/2024
P153875	92956	PIE	10/22/2024
P152540	92281	PIE	10/29/2024
P153855	92943	PIN	10/29/2024
P152528	92275	PIE	10/29/2024
P154257	93151	EVPA	11/05/2024
P153912	92975	PIE	11/05/2024
P153876	92957	PIE	11/05/2024
P153844	92938	PIN	11/06/2024
P154408	93212	EVPA	11/06/2024
P153856	92944	PIN	11/12/2024
P152541	92282	PIE	11/12/2024
P152529	92276	PIE	11/12/2024
P153877	92958	PIE	11/19/2024
P153913	92976	PIE	11/20/2024
P153845	92939	PIN	11/20/2024
P153896	92968	PIE	11/26/2024
P153920	92980	PIE	11/26/2024
P153857	92945	PIN	11/26/2024
P155066	93544	EVPA	12/03/2024
P153914	92977	PIE	12/03/2024
P153878	92959	PIE	12/03/2024
P153846	92940	PIN	12/04/2024
P155074	93548	EVPA	12/04/2024
P153921	92981	PIE	12/10/2024
P153858	92946	PIN	12/10/2024
P153897	92969	PIE	12/11/2024
P153879	92960	PIE	12/18/2024
P153915	92978	PIE	12/18/2024
P153847	92941	PIN	12/18/2024
P153922	92982	PIE	12/27/2024
P153898	92970	PIE	12/27/2024
P153859	92947	PIN	12/27/2024

a. EVPA – Everglades Protection Area; PIE – Everglades National Park Inflows East; and PIN – Everglades National Park Inflows North.

During the 45 sampling events described in **Table 2**, no grab sample record for the projects/locations described in the *Introduction* was identified as no bottle which indicates that a sample was not collected.

FIELD QUALITY CONTROL

Field quality control samples were collected at sampling locations during each sampling event to assess the quality of the sample collection process as required by the *Field Sampling Manual*. The results from these quality control samples were associated with all samples collected during the sampling trip (day). If a specific field quality control sample failed to meet the requirements outlined in the Florida Department of Environmental Protection (FDEP) *Quality Assurance Rule* (Chapter 62-160, Florida Administrative Code [F.A.C.]), qualifiers were added to the appropriate sample results. The types of field quality control samples could include replicate samples (RSs) and field quality control blanks, along with field generated equipment blanks (EBs), field-cleaned equipment blanks (FCEBs), and field blanks (FBs). The sampling events listed in **Table 2** may include field quality control samples collected at locations other than those listed in **Table 1**.

For the 45 sampling events described above, 22 field quality control blanks (one EB, six FBs, 15 FCEBs) and two RSs were collected. One of the 15 FCEBs, which was collected from S-177 (Sample ID: P153868-12), had a concentration equal to or greater than the TP method detection limit (MDL) of 0.002 milligrams per liter (mg/L). One of the 15 FCEBs, with Sample ID P153913-5, was assigned a "J" qualifier due to improper laboratory or field protocol. Project managers responsible for directing the sampling activities may also place qualifiers and/or remark codes on sample results based on project specific requirements, historical results for a given location, issues related to site conditions, and/or problems encountered by technicians when the samples were collected. Remark codes include a project manager remark (PMR), an SFWMD-derived and -applied remark code indicating a potential quality issue not otherwise defined by the qualifiers specified in the FDEP *Quality Assurance Rule* (Chapter 62-160, F.A.C.). No PMR was assigned to field quality control replicate samples that had a concentration equal to or greater than the TP MDL of 0.002 mg/L.

Qualifiers were assigned to samples (**Table 3**): Two "G" qualifiers due to analyte detection at or above the method detection limit (0.002 mg/L) where the associated FCEB value was greater than 10 percent (1/10) of the sample value, and one "J" qualifier because the laboratory analysis was from an improper field protocol per the FDEP *Quality Assurance Rule* (Chapter 62-160, F.A.C.).

Table 3. Results with qualifiers and remark codes during the reporting period for the 45 sample events listed in Table 2.

Work Identifier	Project [a]	Sample Identifier	Station	Collection Date	Qualifier or Remark Code / Reason
92955004	PIE	P153868-4	G737	10/01/2024	G: Field quality control blank detection greater than 10 percent (1/10) of sample value for blank.
92955009	PIE	P153868-9	S18C	10/01/2024	G: Field quality control blank detection greater than 10 percent (1/10) of sample value for blank.
92976003	PIE	P153913-3	S332DX	11/19/2024	J: Estimated value because of improper laboratory or field protocols.

a. PIE – Everglades National Park Inflows East.

FIELD AUDITS

SFWMD did not conduct any field audits on TOC-related projects during the fourth quarter of 2024.

FIELD PROCEDURE UPDATES

No major procedural updates related to TP sample collection were made during the period specified in this report.

LABORATORY ANALYSIS QUALITY ASSESSMENT

SAMPLE ANALYSES

SFWMD Analytical Services Chemistry Laboratory staff conducted 354 TP analyses for the grab samples collected during the 45 sampling events listed in **Table 2** and detailed in RDS. Of those 354 TP results, 153 were for grab samples collected from projects/locations listed in **Table 1** (excluding field quality control samples). For reference, a complete set of all 354 grab TP results can be found in the RDS described in **Table 1** with the sample identifiers, sampling locations, collection dates, etc.

LABORATORY QUALITY CONTROL

TP analyses are routinely conducted in the SFWMD Analytical Services Chemistry Laboratory in analytical batches of approximately 100 samples. To assess the quality of the sample results produced during the analyses of these batches, various types of laboratory control samples are included according to the requirements described in the *Chemistry Laboratory Quality Manual* (SFWMD-LAB-QM-001). The results of these laboratory quality control samples are associated with the analyses conducted in each batch, and qualifiers are added to the data as required by the FDEP *Quality Assurance Rule* (Chapter 62-160, F.A.C.), which is based on the specifications found in the *Chemistry Laboratory Quality Manual* (SFWMD-LAB-QM-001). The types of laboratory quality control samples typically run in a batch include samples with certified concentrations (laboratory control samples), matrix spikes, precision checks (duplicates or matrix spike duplicates), and method blanks. Since the laboratory exhibited no quality control failures for batches associated with the RDS, none of the laboratory operation related qualifiers were added for the 153 TP results of samples collected from projects/locations listed in **Table 1**.

METHOD DETECTION LIMIT AND PRACTICAL QUANTITATION LIMIT

The MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined by the laboratory on an annual basis using the procedure described in the Code of Federal Regulations (CFR), 40 CFR 136, Appendix B. The practical quantitation limit (PQL) is the minimum concentration of an analyte that can be measured with a high degree of confidence that the analyte is present at or above that concentration. However, there is not any universally accepted (or required) method for determining the PQL. In the case of TP analyses, the SFWMD Analytical Services Chemistry Laboratory PQL (0.004 mg/L) is set to the concentration of the lowest standard used for calibration, which is a typical approach among analytical laboratories. Any TP results that are below the MDL (0.002 mg/L) are assigned a “U” qualifier indicating that there is high confidence that the analyte is not present. The reported TP values between the MDL (0.002 mg/L) and the PQL (0.004 mg/L) are assigned an “I” qualifier, indicating that the results are at concentrations that cannot be accurately quantified. Of the 153 TP results reported, no results were below the MDL and six samples had concentrations between the MDL (0.002 mg/L) and the PQL (0.004 mg/L).

ESTIMATION OF ANALYTICAL MEASUREMENT UNCERTAINTY

All measurements are subject to uncertainty and a measured value is only complete if a statement of the associated uncertainty accompanies it. The definition of uncertainty (of measurement) can be found in the *International Vocabulary of Basic and General Standard Terms in Metrology*: "A parameter associated with the result of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the measurand" (JCGM 1993). The uncertainty has a probabilistic basis and reflects incomplete knowledge of the quantity. The SFWMD Analytical Services Chemistry Laboratory provides uncertainty estimates using the nested hierarchical methodology by Ingersoll (2001) in combination with a mathematical model found in Eurachem/CITAC (2012). This quality control-based nested approach uses the statistical quality control data attributed to laboratory measurement activities and does not include uncertainty attributed to field sampling activities. The estimated uncertainty is calculated using the following equation:

$$\mathbf{U(x)} = \sqrt{S_o^2 + (S_1^2 x^2)}$$

U(x) is the combined standard uncertainty in the result x at the 95% confidence interval (CI).
$\mathbf{S_0}$ is a constant contribution to the overall uncertainty derived from the procedure to determine the MDL.
$\mathbf{S_1}$ is a proportionality constant derived from nested hierarchical methodology by Ingersoll (2001).

During this reporting period, the uncertainty constants are $\mathbf{S_0}$ = 0.002 and $\mathbf{S_1}$ = 0.068. Estimated uncertainties are calculated automatically by LIMS using the equation and constants shown above and are provided with all TP results. **Figure 1** presents estimated uncertainties at the 95% and 99% CIs relative to the MDL and PQL of the TP measurement process.

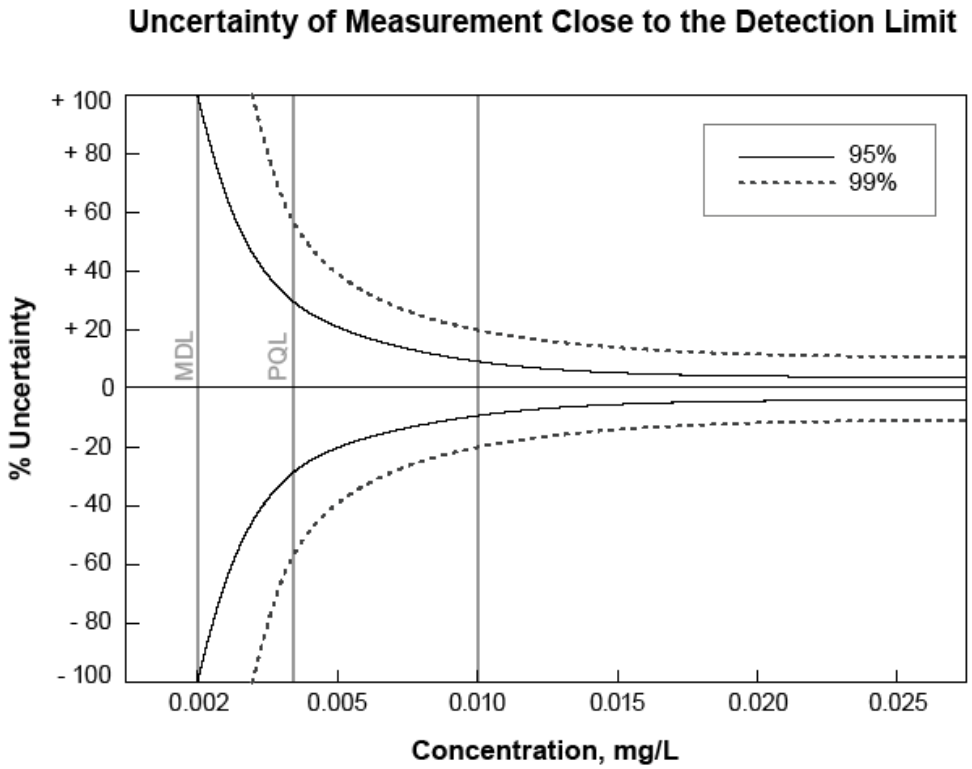

Figure 1. Estimated uncertainties at 95% and 99% CIs relative to the MDL and PQL of the TP measurement process.

As seen in **Figure 1**, the percentage measurement uncertainty (95% CI) is 100% at MDL, nearly 30% at PQL, and remains relatively constant at higher concentrations.

PROFICIENCY TESTING AND PERFORMANCE EVALUATION

The SFWMD Analytical Services Chemistry Laboratory participates in a variety of studies to evaluate the proficiency of the laboratory's quality system. During the fourth quarter of 2024, the laboratory received TP results from one performance evaluation study, Phenova #WP1024.The reported result was evaluated as "acceptable" with a calculated Z-score of 0.011.

LABORATORY AUDITS

During this reporting period no quality system laboratory audits were conducted.

PROCEDURE UPDATES

The TP sample preparation (Standard Method 4500-P B (5)-2011, Persulfate Digestion Method) and analytical procedure (Standard Method 4500-P H-2011, Automated Ascorbic Acid Reduction Method) did not change during this reporting period.

REFERENCES

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SFWMD. *Chemistry Laboratory Quality Manual*. SFWMD-LAB-QM-001, most current, effective version. South Florida Water Management District, West Palm Beach, FL.

SFWMD. Field Quality Manual. SFWMD-FIELD-QM-001, most current, effective version. South Florida Water Management District, West Palm Beach, FL.

SFWMD. Field Sampling Manual. SFWMD-FIELD-FSM-001, most current, effective version. South Florida Water Management District, West Palm Beach, FL.

SFWMD. Standard Operating Procedure for the Determination of Total and Dissolved Phosphorus. SFWMD-LAB-SOP-3140, most current, effective version. South Florida Water Management District, West Palm Beach, FL.

GLOSSARY

Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components that are due to sampling and analytical operations.

Confidence Interval (CI): A range of values so defined that there is a specified probability that the value of a parameter lies within it.

Equipment Blank (EB): Field quality control sample prepared using sampling equipment that has been brought to the site or processing area precleaned and is collected before the equipment has been used. The results of these blanks are used to monitor the on-site sampling environment, sampling equipment decontamination, sample container cleaning, suitability of sample preservatives and analyte-free water, sample transport and storage conditions, and laboratory process.

Field Blank (FB): FBs are collected by pouring analyte-free water directly into the sample container, preserved, and kept open for the same approximate time and interval as required for collection and/or processing of the routine sample. The results of this blank are used to monitor the on-site sampling environment, sample container cleaning, the suitability of sample preservatives and analyte-free water, sample transport and storage conditions, and laboratory process.

Field Cleaned Equipment Blank (FCEB): Field quality control sample prepared using sampling equipment that has been cleaned in the field or in the processing area. The results of this blank are used to monitor the on-site sampling environment, sampling equipment field decontamination, sample container cleaning, suitability of sample preservatives and analyte-free water, sample transport and storage conditions, and laboratory process.

Measurand: Particular quantity subject to measurement.

Method Detection Limit (MDL): The smallest concentration of an analyte of interest that can be measured and reported with 99% confidence that the concentration is greater than zero. The MDLs are determined from the analysis of a sample in a given matrix, using accepted sampling and analytical preparation procedures, containing the analyte at a specified level. The MDL is determined by the protocol defined in the Code of Federal Regulations (CFR) Section 40 CFR, Part 136, Appendix B, as established by the United States Environmental Protection Agency.

Practical Quantitation Limit (PQL): The smallest concentration of an analyte of interest that can be quantitatively reported with a specific degree of confidence. The PQL is verified for each matrix, technology, and analyte. The validity of the PQL is verified by analysis of a quality control sample containing the analyte of concern.

Precision: The agreement or closeness between two or more results is an indication that the measurement system is operating consistently and is a quantifiable indication of variations introduced by the analytical systems over a given time and field sampling period.

Replicate Sample (RS): An RS is collected by repeating (simultaneously or in rapid succession) the entire sample acquisition technique that was used to obtain the routine sample. A single RS set (e.g., one sample and two RSs) is collected per quarter, per project, at the same station, for the longest parameter list. RS data are compared to routine sample data to evaluate sampling precision.

Uncertainty: The range of values within which the true value is estimated to lie. It is a best estimate of possible inaccuracy due to both random and systematic error.

Z-Score: A measure of the deviation of the result (Xi) from the assigned value (X) for that determinant (calculated as $z = (Xi - X)/\sigma$, where σ is a standard deviation) (Eurachem/CITAC 2012).